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(54) Title: LOW TEMPERATURE INITIATORS FOR FLUOROOLEFIN POLYMERIZATION

(57) Abstract: Diacyl peroxides having the structure (I):  $R_1CXX'(CYY')_eCF_2(C=O)OO(C=O)CF_2CWW'(CZZ')_fR_2$ , wherein e and e' are independently 0 or 1; and when e=0, at least one of X, X' is H and any of the other X, X' is H or F; when e'=0, at least one of W, W' is H and any of the other W, W' is H or F; when e=1, at least one of X, X', Y, Y' is H and any of the other X, X', Y, Y' is H or F; when e'=1, at least one of W, W', Z, Z' is H and any of the other W, W', Z, Z' is H or F; wherein  $R_1=C_nF_{(2n+1)}$ , n=1 to 4, and wherein  $R_2=C_mF_{(2m+1)}$ , m=1 to 4, are low temperature initiators for fluoroolefin polymerization.

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TITLE  
 LOW TEMPERATURE INITIATORS FOR  
 FLUOROOLEFIN POLYMERIZATION  
FIELD OF THE INVENTION

5 A new class of low temperature initiators has been found,  
 $C_nF_{2n+1}(CH_2)_aCF_2(C=O)O-O(C=O)CF_2(CH_2)_bC_mF_{2m+1}$ , wherein n and m are  
 each independently 1 to 4, and a and b are each independently 1 or 2, enabling  
 fluoroolefin polymerizations at relatively low temperatures.

TECHNICAL BACKGROUND

10 Diacyl peroxides of diverse structure have been patented as fluoroolefin  
 polymerization initiators, for example,  $[RO(CH_2CF_2CF_2O)_nCH_2CF_2(C=O)O-]_2$ ,  
 U.S. Patent 4,663,407, issued May 1987, to Daikin Industries,  
 $[-O(C=O)CFR_f(C_3F_6O)_h(C_2F_4O)_m(CF_2O)_n(C_6F_{12}O)_aCFR_f(C=O)O-]_x$ , U.S.  
 Patent 3,882,193 (issued May 6, 1975 to Minnesota Mining and Manufacturing  
 15 Company);  $[X(CF_2)_n(C=O)O-]_2$ , U.S. Patent 3,528,954 (issued September 15,  
 1970 to E. I. du Pont de Nemours and Company);  
 $XC_mF_{2m}(C=O)OO(C=O)C_nF_{2n}X$ , EP 0606 492 A1 (published July 9, 1993, to  
 Daikin Industries) and  $Cl_2FC(C=O)OO(C=O)CCl_2F$  U.S. Patent 5,569,728  
 (issued October 29, 1996, to Ausimont, SpA.). The best diacyl peroxide for a  
 20 particular application can often be determined by its half-life. By "half-life" we  
 mean the elapsed time it takes for half of the initiator in a system to decompose  
 thermally to radicals. An initiator needs to last long enough for homogeneous  
 mixing to occur with monomer but not so long as to make polymerization  
 uneconomically slow. Half-lives on the order of 15 minutes to several hours are  
 25 desirable.

Polymerization temperature can affect fundamental aspects of final  
 polymer structure such as molecular weight and branching. Thus, a preferred  
 polymerization temperature is chosen first and an initiator with an appropriate  
 half-life chosen second. As used herein "HFPO is hexafluoropropylene oxide.  
 30 For example were a polymerization's temperature set to 30°C, dimer peroxide  
 (DP) with a half-life of 0.98 hours would be a faster and better choice than  
 heptafluorobutyryl peroxide (4P) with a half-life of 8.8 hours (Table 1). If,  
 however, the same polymerization needed to be run at 0°C, the half-life of DP  
 would increase to 64 to 92 hours (Table 1), threatening an uneconomically slow  
 35 process.

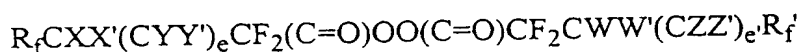
The potential advantages of faster, lower temperature initiation include  
 increased productivity, increased polymer linearity, decreased chain transfer,  
 increased polymer molecular weight, decreased monomer oligomerization during

product letdown, decreased acid fluoride end group formation in the polymer, and decreased reactor pressure in condensed media such as liquified hexafluoropropylene (HFP) or CO<sub>2</sub>. The fastest (i.e., lowest temperature), well documented prior art diacyl peroxide, 1H3P, has a 16 hour half-life at 10°C (see Table 1, J. Org. Chem., 47, 2009 (1982) and Japanese Pat. 61152653 A2, Chem. Abstracts 106:120380). Trichloroacetyl peroxide, which has been reported to have a 10 hour half-life at -3.9°C (see U. S. Patent No. 5,688,838) is still faster than 1H3P ("HCF<sub>2</sub>CF<sub>2</sub>-") but has two disadvantages. First, the -CCl<sub>3</sub> group tends to chain transfer and, second, the initiating Cl<sub>3</sub>C\* radical remains attached to the polymer chain as a potentially unstable end group. At 10°C, the inventive bis(2,2,5,5,5-pentafluoropentanoyl) peroxide (hereinafter "4H5P") and bis(2,2,5,5,6,6,7,7,8,8,8-undecafluorooctanoyl) peroxide (hereinafter "4H8P") initiators disclosed herein are 13 times faster and 9 times faster, respectively, than 1H3P. Holding the rate of radical generation constant, this represents a 10°C to 20°C advantage in polymerization temperature for the inventive peroxides of the present invention. Unlike trichloroacetyl peroxide, 4H5P and 4H8P will not introduce undesirable chlorine into either the polymer or the reaction mixture. Thus 4H5P, 4H8P, and the related peroxides disclosed herein appear particularly attractive as low temperature fluoroolefin polymerization initiators.

Commonly owned U.S. Patent No. 5,763,552 discloses partially fluorinated surfactants of the formula R<sub>f</sub>-(CH<sub>2</sub>)-z-R<sub>f</sub> COOH useful in the polymerization of fluorinated monomers. These surfactants are synthetic precursors, several steps removed, for many of the diacyl peroxides disclosed herein.

## SUMMARY OF THE INVENTION

Disclosed in this invention are diacyl peroxides having the structure I,



I

30

wherein e and e' are independently 0 or 1; and

when e = 0, at least one of X, X' is H and any of the other X, X' is H or F; when e' = 0, at least one of W, W' is H and any of the other W, W' is H or F;

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when e = 1, at least one of X, X', Y, Y' is H and any of the other X, X', Y, Y' is H or F;

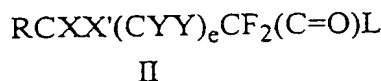
when e' = 1, at least one of W, W', Z, Z' is H and any of the other W, W', Z, Z' is H or F;

wherein  $R_f = C_nF_{(2n+1)}$ ,  $n = 1$  to  $4$ ; and

wherein  $R_f = C_mF_{(2m+1)}$ ,  $m = 1$  to  $4$ .

Also disclosed is a method for preparing a new class of diacyl peroxides, comprising:

5 contacting at least one acid halide of the formula II

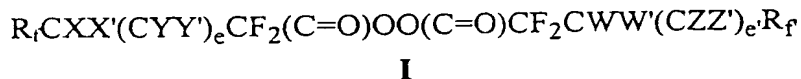


10 wherein  $e = 0$  or  $1$ , and when  $e = 0$ , at least one of  $X, X'$  is  $H$  and any of the other  $X, X'$  is  $H$  or  $F$ , and when  $e = 1$ , at least one of  $X, X', Y, Y'$  is  $H$  and any of the other  $X, X', Y, Y'$  is  $H$  or  $F$ ;

wherein  $L$  is  $Cl$  or  $F$ , and

15 wherein  $R$  is  $R_f$  or  $R_f$ ; and wherein  $R_f = C_nF_{(2n+1)}$ ,  $n = 1$  to  $4$  and  $R_f = C_mF_{(2m+1)}$ ,  $m = 1$  to  $4$ ;

with a peroxide, to generate a diacyl peroxide of the structure



20

wherein  $e$  and  $e'$  are independently  $0$  or  $1$ ; and

when  $e = 0$ , at least one of  $X, X'$  is  $H$  and any of the other  $X, X'$  is  $H$  or  $F$ ; when  $e' = 0$ , at least one of  $W, W'$  is  $H$  and any of the other  $W, W'$  is  $H$  or  $F$ ;

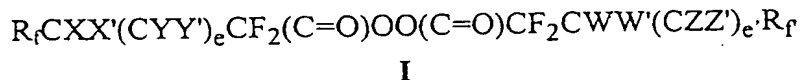
25 when  $e = 1$ , at least one of  $X, X', Y, Y'$  is  $H$  and any of the other  $X, X', Y, Y'$  is  $H$  or  $F$ ;

when  $e' = 1$ , at least one of  $W, W', Z, Z'$  is  $H$  and any of the other  $W, W', Z, Z'$  is  $H$  or  $F$ ;

wherein  $R_f = C_nF_{(2n+1)}$ ,  $n = 1$  to  $4$ ; and

30 wherein  $R_f = C_mF_{(2m+1)}$ ,  $m = 1$  to  $4$ .

A further disclosure of this invention is a method for using a diacyl peroxide of the structure I, comprising:



35

wherein  $e$  and  $e'$  are independently  $0$  or  $1$ ; and

when  $e = 0$ , at least one of  $X, X'$  is  $H$  and any of the other  $X, X'$  is  $H$  or  $F$ ; when  $e' = 0$ , at least one of  $W, W'$  is  $H$  and any of the other  $W, W'$  is  $H$  or  $F$ ;

40

when  $e = 1$ , at least one of  $X, X', Y, Y'$  is H and any of the other  $X, X', Y, Y'$  is H or F;

when  $e' = 1$ , at least one of  $W, W', Z, Z'$  is H and any of the other  $W, W', Z, Z'$  is H or F;

5 wherein  $R_f = C_nF_{(2n+1)}$ ,  $n = 1$  to 4; and

wherein  $R_f = C_mF_{(2m+1)}$ ,  $m = 1$  to 4

(i) contacting at least one diacyl peroxide having the structure I with a monomer;

(ii) optionally, in the presence of a reaction medium selected from the group consisting of fluorocarbon, chlorofluorocarbon, and hydrocarbon fluids; fluorocarbon, chlorofluorocarbon and hydrocarbon mixed with water, wherein hybrid polymerization conditions form; and liquid or supercritical carbon dioxide; and

(iii) polymerizing the monomer, under suitable polymerization temperature and pressure whereby fluoroolefin polymerization occurs.

Another disclosure of this invention is a process for fluoroolefin polymerization, comprising the steps of:

(i) contacting at least one diacyl peroxide having the structure I

20 
$$R_fCXX'(CYY')_eCF_2(C=O)OO(C=O)CF_2CWW'(CZZ')_{e'}R_f$$

I

wherein  $e$  and  $e'$  are independently 0 or 1; and

when  $e = 0$ , at least one of  $X, X'$  is H and any of the other  $X, X'$  is H or F; when  $e' = 0$ , at least one of  $W, W'$  is H and any of the other  $W, W'$  is H or F;

when  $e = 1$ , at least one of  $X, X', Y, Y'$  is H and any of the other  $X, X', Y, Y'$  is H or F;

when  $e' = 1$ , at least one of  $W, W', Z, Z'$  is H and any of the other  $W, W', Z, Z'$  is H or F;

30 wherein  $R_f = C_nF_{(2n+1)}$ ,  $n = 1$  to 4; and

wherein  $R_f = C_mF_{(2m+1)}$ ,  $m = 1$  to 4;

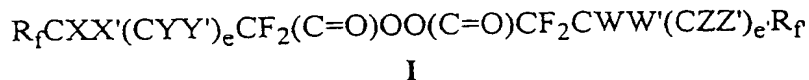
with a monomer;

(ii) optionally, in the presence of a reaction medium selected from the group consisting of fluorocarbon, chlorofluorocarbon, hydrocarbon fluids; fluorocarbon, chlorofluorocarbon and hydrocarbon mixed with water, wherein hybrid polymerization conditions form; and liquid or supercritical carbon dioxide; and

(iii) polymerizing the monomer, under suitable polymerization temperature and pressure whereby fluoroolefin polymerization occurs.

This invention also discloses a product of the process for fluoroolefin polymerization, wherein said process comprises the steps of:

- 5 (i) contacting at least one diacyl peroxide having the structure I



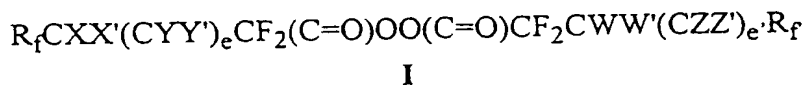
- 10 wherein e and e' are independently 0 or 1; and  
 when e = 0, at least one of X, X' is H and any of the other X, X' is H or F;  
 when e' = 0, at least one of W, W' is H and any of the other W, W' is H or F;  
 when e = 1, at least one of X, X', Y, Y' is H and any of the other X, X',  
 Y, Y' is H or F;  
 15 when e' = 1, at least one of W, W', Z, Z' is H and any of the other W,  
 W', Z, Z' is H or F;  
 wherein  $R_f = C_n F_{(2n+1)}$ , n = 1 to 4; and  
 wherein  $R_{f'} = C_m F_{(2m+1)}$ , m = 1 to 4;  
 with a monomer;

- 20 (ii) optionally, in the presence of a reaction medium selected from the group consisting of fluorocarbon, chlorofluorocarbon, hydrocarbon fluids; fluorocarbon, chlorofluorocarbon and hydrocarbon mixed with water, wherein hybrid polymerization conditions form; and liquid or supercritical carbon dioxide; and

- 25 (iii) polymerizing the monomer, under suitable polymerization temperature and pressure whereby fluoroolefin polymerization occurs.

#### DETAILS OF THE INVENTION

- This invention relates to the synthesis of a novel class of diacyl peroxides which are effective low temperature polymerization initiators for nonaqueous and  
 30 hybrid polymerization conditions, including the use of CO<sub>2</sub> as a polymerization solvent. By "hybrid polymerization conditions" is meant mixed aqueous and non-aqueous solvents. Disclosed in the invention are diacyl peroxides of the structure



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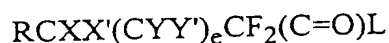
- wherein e and e' are independently 0 or 1; and  
 when e = 0, at least one of X, X' is H and any of the other X, X' is H or F;  
 when e' = 0, at least one of W, W' is H and any of the other W, W' is H or F; when

$e = 1$ , at least one of  $X, X', Y, Y'$  is H and any of the other  $X, X', Y, Y'$  is H or F;  
when  $e' = 1$ , at least one of  $W, W', Z, Z'$  is H and any of the other  $W, W', Z, Z'$  is H  
or F;

wherein  $R_f = C_n F_{(2n+1)}$ ,  $n = 1$  to 4, preferably 1 or 4; and

5 wherein  $R_f = C_m F_{(2m+1)}$ ,  $m = 1$  to 4, preferably 1 or 4.

These peroxides are synthesized from one or more acid halides of the  
formula



II

10 wherein  $e = 0$  or 1, and when  $e = 0$ , at least one of  $X, X'$  is H and any of  
the other  $X, X'$  is H or F, and when  $e = 1$ , at least one of  $X, X', Y, Y'$  is H and any  
other of the other  $X, X', Y, Y'$  is H or F;

15 wherein L is Cl or F, and

wherein R is  $R_f$  or  $R_f$  as described above.

For example starting with two different acid halides  $R_f CXX'(CYY')_e CF_2(C=O)L$   
gives not only the two symmetrical peroxides but the unsymmetrical peroxides as  
well. The acid chlorides or acid fluorides are subsequently reacted with peroxides  
20 such as, but not limited to,  $H_2O_2$  in the presence of a base,  $Na_2O_2$ , and  $K_2O_2$  to  
form the desired peroxide compounds. Examples of useful bases are, but not  
limited to, NaOH, KOH,  $Na_2CO_3$ , and  $K_2CO_3$ . This is demonstrated in the  
Examples below. When increased peroxide solubility in the reaction solvent is  
desired, mixtures of two or more acid halides can be used. The product in such  
25 cases includes unsymmetrical peroxides.

The preparation of initiators of this invention can be facilitated by a variety  
of processes, including high intensity mixing processes as described in U.S. Patent  
No. 5,831,131, incorporated herein by reference. High intensity ultrasonic mixing  
was used to make the peroxides of Examples 1B, 2B and 2C described below.

30 One advantage of ultrasonic mixing is the simplicity and speed of the synthetic  
method. Other synthetic methods can also be used, including stirring as disclosed  
in Z. Chengxue et al., *J. Org. Chem.*, **47**, 2009 (1982), and making a nearly water-  
free slurry as disclosed in U.S. Patent No. 5,021,516. Any of the synthetic  
methods commonly used to make diacyl peroxides generally from acid halides can  
35 be used in the present invention. A general reference describing these methods is  
found in S. R. Sandler and W. Karo, *Polymer Syntheses, Vol. 1*, Academic Press,  
New York, 1974, Chapter 14.

Considering that 2, 3, 4, and 5, defined below in Table 2, decompose much faster than 4P 7, we conclude that having C-H bonds two or three carbons removed from the peroxide carbonyl greatly accelerates peroxide decomposition.

Vinyl monomers are generally useful for polymerization according to this invention. Preferably, these monomers are fluorocarbon, chlorofluorocarbon and hydrofluorocarbon vinyl olefins or vinyl ethers that homopolymerize, copolymerize, or copolymerize with hydrocarbon monomers such as ethylene and propylene, which are known to copolymerize with fluoroolefins. The monomers tetrafluoroethylene (TFE), perfluoro(propylene vinyl ether) (PPVE), perfluoro(methyl vinyl ether) (PMVE), perfluoro(ethyl vinyl ether) (PEVE), 4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole(PDD), hexafluoropropylene (HFP),  $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$  (PSEPVE) and  $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{SO}_2\text{R}$ , vinylidene fluoride ( $\text{VF}_2$ ), vinyl fluoride, trifluoroethylene,  $\text{CF}_2\text{CFOCF}_2\text{CFCF}_3\text{OCF}_2\text{CF}_2\text{CN}$  (8-CNVE), chlorotrifluoro ethylene (CTFE),  $(\text{CF}_3)_2\text{C}=\text{CH}_2$ , and vinyl acetate (VAc) are most preferably employed.

A variety of polymer products can be formed from the monomers employed. These are well known to those skilled in the art. See, for example, Kirk-Othmer Encyclopedia of Chemical Technology, 4<sup>th</sup> edition, Wiley-Interscience, New York, 1994, Vol. 11, pp. 621-729; H. Mark et al, Encyclopedia of Polymer Science and Engineering, 2<sup>nd</sup> edition, Wiley-Interscience, New York, 1987, Vol. 7, pp. 256-269 and 1989, Vol. 16, pp. 577-640; and J. Schiers, ed., Modern Fluoropolymers, John Wiley and Sons, New York, 1997.

The processes of this invention can take place in a variety of reaction media. These media include fluorocarbon, chlorofluorocarbon and hydrocarbon fluids; fluorocarbon, chlorofluorocarbon and hydrocarbon fluids mixed with water to form hybrid polymerization conditions; and liquid and supercritical carbon dioxide.

The diacyl peroxides of the present invention permit fluoroolefin polymerizations at lower temperatures. The initiation temperatures for the reactions of the present invention can range from about -20°C to 30°C, preferably -10°C to 20°C, and most preferably 0°C to 10°C.

The polymerization process of the present invention offers a number of potential advantages, including increased productivity, increased linearity, faster reaction time, increased molecular weight, decreased monomer oligomerization during letdown, decreased acid fluoride end group formation, and decreased reactor pressure in condensed media such, as liquified HFP or  $\text{CO}_2$ .



Peroxide Titration

The peroxide titration used in the Examples follows. In a loosely stoppered Erlenmeyer flask several grams of dry ice are added to 25 ml of glacial acetic acid, so as to flush oxygen from the system. Five ml of a solution of 30 g of KI in 70 ml of deoxygenated water was added, and then 5.0 ml of the peroxide solution to be analyzed. The mixture was stirred for 30 minutes to allow the peroxide to react with the iodide. One hundred ml of deoxygenated water was added and the deep iodine color was titrated to light yellow with 0.1N sodium thiosulfate. Then 0.5 g of "Thyodene" (purchased from Fisher Scientific Co.) iodometric indicator was added making the reaction mixture turn blue. Titration was completed by bringing to a colorless endpoint with additional 0.1N sodium thiosulfate. Molar peroxide concentration was calculated by multiplying 0.01 by the total number of ml of sodium thiosulfate solution.

EXAMPLES

Unless otherwise specified, all chemicals and reagents were used as received from Aldrich Chemical Company, Milwaukee, WI.

EXAMPLE 1Preparation and Use of 4H8P 3

The starting material for this example, 2,2,5,5,6,6,7,7,8,8,8-Undecafluorooctanoic acid, was prepared by the method described in U.S. Patent No. 5,763,552, incorporated herein by reference.

A. Preparation of  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CF}_2(\text{C}=\text{O})\text{Cl}$ , 2,2,5,5,6,6,7,7,8,8,8-undecafluorooctanoyl chloride, ( $\text{C}_8\text{F}_9\text{-CH}_2\text{CH}_2\text{-CF}_2\text{-COCl}$ ) (4H8CI):

2,2,5,5,6,6,7,7,8,8,8-Undecafluorooctanoic acid (50 g, 0.146 mol) was dissolved in methylene chloride (250 mL). Pyridine (4.62 g, 0.0584 mol) and oxalyl chloride (22.3 g, 0.175 mol) were added in sequence, a slight exotherm was observed. The reaction mixture was refluxed for overnight (ca. 16 hrs) and the methylene chloride solvent was removed *in vacuo* after cooling. Ether was then added into the residue and the solution was filtered to remove the insoluble solid salt. After removing the ether solvent the residue was distilled to afford the title compound as a clear, colorless liquid, bp. 41-42°C/10 mm Hg, yield 29.5 g (56%); repeated run gave a 70% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.39 (m, 2H), 2.47 (m, 2H);  $^{19}\text{F}$  NMR (282.75 MHz,  $\text{CDCl}_3$ ): -81.6 (m, 3F), -103.2 (t, J = 15.8 Hz, 2F), -115.2 (t, J = 14.8 Hz, 2F), -124.7 (m, 2F), -126.5 (m, 2F); IR (neat): 1800  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_8\text{H}_4\text{F}_{11}\text{ClO}$ : C: 26.65, H: 1.12, Cl: 9.83; Found: C: 26.61, H: 1.07, Cl: 9.66; Mass for  $[\text{M-COCl}]$ : Calc: 297.0137; Found: 297.0172.

B. Preparation of 4H8P 3

A wet-ice, chilled 150 ml beaker was loaded with 1.5 g of 85% potassium hydroxide pellets (23 mmoles) dissolved in 5 ml distilled water, 78 ml of Freon<sup>®</sup> E1 (CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>HCF<sub>3</sub>), and 2.35 ml of 30% aqueous hydrogen peroxide (23 mmoles). A nominal 100 watt titanium ultrasonic horn was lowered into the reaction mixture and then 6.5 g of 4H8Cl (18 mmoles) added all at once. After an additional 30 seconds of ultrasonication, the reaction mixture was transferred to a separatory funnel prechilled to ~-15°C. The lower organic phase, still a bit hazy, was quickly separated and its volume measured as 74 ml. After sitting about 10 minutes at ~0°C, iodometric titration found the concentration of 4H8P 3 to be 0.076 M for a yield of 62% based on starting acid chloride 4H8Cl.

C. Initiation of TFE Polymerization, Nonaqueous Fluorocarbon Solvent

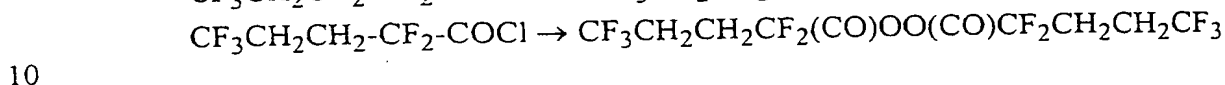
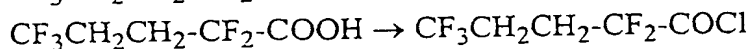
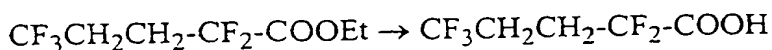
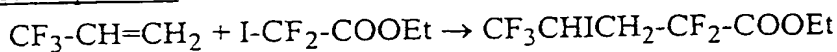
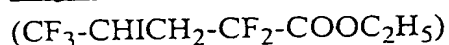
A prechilled 400 ml autoclave was loaded with 100 ml Freon<sup>®</sup> 113 (CF<sub>2</sub>ClCCl<sub>2</sub>F) and 5 ml of the 0.076 M 4H8P 3 solution prepared above. The autoclave was evacuated, filled with 50 g of tetrafluoroethylene (TFE) and allowed to warm towards room temperature. After initial loading at 82 psi at -44°C, pressure steadily dropped during warm up hitting 56 psi at -15°C and 24 psi at 23°C at the end of the warmup ~10 hours later. Filtration, washing, and drying gave 43 g of white poly(tetrafluoroethylene).

D. Initiation of TFE/PPVE Copolymerization, Nonaqueous Fluorocarbon Solvent

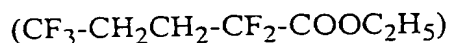
A prechilled 400 ml autoclave was loaded with 100 ml Freon<sup>®</sup> 113 (CF<sub>2</sub>ClCCl<sub>2</sub>F) and 5 ml of the 0.076 M 4H8P 3 solution prepared above. The autoclave was evacuated, filled with 50 g of tetrafluoroethylene (TFE) and 5 g of perfluoro(propyl vinyl ether) and allowed to warm towards room temperature. After initial loading at 125 psi at -35°C, pressure decreased to 106 psi at 7°C and finished at 22 psi at 24°C at the end of the warmup ~10 hours later. Filtration, washing, and drying gave 48.6 g of white tetrafluoroethylene/perfluoro(propyl vinyl ether) copolymer.

E. Initiation of TFE Polymerization, Mixed Aqueous/Fluorocarbon Solvent

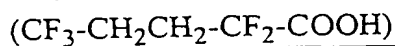
A prechilled 400 autoclave was loaded with 100 ml ice cold water and 5 ml of 0.095 M 4H8P 3 solution in CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>HCF<sub>3</sub>. The autoclave was evacuated, filled with 50 g of tetrafluoroethylene (TFE) and allowed to warm towards room temperature. After initial loading at 230 psi at -0.3°C, pressure steadily dropped during warm up hitting 178 psi at 19°C and 32 psi at 30°C at the end of the warmup ~7 hours later. Filtration, washing, and drying gave 43 g of white poly(tetrafluoroethylene).

EXAMPLE 2Preparation and Use of 4H5P 2Chemical EquationsA. Preparation of ethyl 4-iodo-2,2,5,5,5-pentafluoropentanoate

In a 400 mL stainless steel autoclave was charged 3,3,3-trifluoro-1-propene ( $\text{CF}_3\text{-CH=CH}_2$ , 42 g, 0.42 mol) and ethyl iododifluoroacetate ( $\text{I-CF}_2\text{-COOC}_2\text{H}_5$ , 100 g, 0.40 mol). The tube was sealed and heated at 200°C for 8 hr under agitation. After cooling the product mixture was distilled to afford the title product as a clear, pale pink liquid. Yield 96 g (69.4%), bp. 47-50°C/1 mm Hg.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.42 (m, 1H), 4.35 (q,  $J = 7$  Hz, 2H), 3.03 (m, 1H), 2.96 (m, 1H), 1.40 (t,  $J = 7$  Hz, 3H);  $^{19}\text{F}$  NMR (282.75 MHz,  $\text{CDCl}_3$ ): -70.5 (dm, 3F), -105.8 (qm, 2F).

B. Preparation of ethyl 2,2,5,5,5-pentafluoropentanoate

The compound ethyl 4-iodo-2,2,5,5,5-pentafluoropentanoate prepared from above experiment (86.5 g, 0.25 mol) was added dropwise into a well-stirred tributyltin hydride liquid (75.5 g, 0.26 mol). The reaction temperature was controlled at below 30°C with external cooling during the process. After addition was complete, the mixture was stirred at 50°C for 2 hr. The product was isolated by distillation, 42.0 g (76.4% yield) of product was obtained as a clear, colorless liquid, bp. 38-39°C/10 mm Hg.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.35 (q,  $J = 7$  Hz, 2H), 2.35 (m, 4H), 1.38 (t,  $J = 7$  Hz, 3H);  $^{19}\text{F}$  NMR (282.75 MHz,  $\text{CDCl}_3$ ): -67.3 (m, 3F), -107.5 (m, 2F).

C. Preparation of 2,2,5,5,5-pentafluoropentanoic acid

Ethyl 2,2,5,5,5-pentafluoropentanoate (140 g, 0.636 mol) was mixed with concentrated hydrochloric acid (350 mL) under nitrogen atmosphere, and was heated at 100-110°C under vigorous stirring. The progress of the reaction was monitored by gas chromatography and the reaction was stopped after 72 hrs. After cooling the bottom organic layer was separated and distilled to afford the desired

acid product (104.7 g, 86% yield) as a clear, colorless liquid, bp. 68-69°C/10 mm Hg.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.60 (s, 1H, -COOH), 2.20 (m, 4H);  $^{19}\text{F}$  NMR (282.75 MHz,  $\text{CDCl}_3$ ): -67.4 (t,  $J = 9$  Hz, 3F), -108.2 (m, 2F).

5 D. Preparation of  $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_2(\text{C}=\text{O})\text{Cl}$ , 2,2,5,5,5-pentafluoropentanoyl chloride; ( $\text{CF}_3\text{-CH}_2\text{CH}_2\text{-CF}_2\text{-COCl}$ ) (4H5Cl)

2,2,5,5,5-pentafluoropentanoic acid (96 g, 0.5 mol) was dissolved in methylene chloride (400 mL). Pyridine (15.8 g, 0.2 mol) and oxalyl chloride (76.2 g, 0.6 mol) were slowly added in sequence into the above solution while the reaction temperature was kept at  $\leq 25^\circ\text{C}$ . After the addition was complete, the  
10 reaction mixture was stirred at ambient temperature for 48 hrs. The methylene chloride solvent was removed by distillation and vacuum was applied so that the volatile product was separated from the residue and was collected in a dry ice-acetone bath cold trap. Re-distillation gave the desired compound as a clear, colorless liquid, bp. 95-97°C, yield 65 g (62%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  
15  $\delta$  2.40 (m, 4H);  $^{19}\text{F}$  NMR (282.75 MHz,  $\text{CDCl}_3$ ): -64.9 (t,  $J = 9.4$  Hz, 3F), -100.6 (m, 2F).

E. Preparation of 4H5P 2 in  $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCFHCFCF}_3$

A wet-ice/acetone chilled 150 ml beaker was loaded with 3.17 g of potassium carbonate (23 mmol) dissolved in 5 ml distilled water, 78 ml of  
20 Freon® E1 ( $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCFHCFCF}_3$ ), and 2.35 ml of 30% aqueous hydrogen peroxide (23 mmol). A nominal 100 watt titanium ultrasonic horn was lowered into the reaction mixture now chilled to  $-2^\circ\text{C}$  and then 4.20 g of 4H5Cl (20 mmol) added all at once. After an additional 60 seconds of ultrasonication, the reaction mixture had reached  $10^\circ\text{C}$  and was transferred to a separatory funnel  
25 prechilled to  $\sim -15^\circ\text{C}$ . The lower organic phase, still a bit hazy, was separated and its volume measured as 74 ml. Iodometric titration found the concentration of 4H5P 2 to be 0.102 M for a yield of 75% based on starting acid chloride 4H5Cl.

F. Preparation of 4H5P 2 in  $\text{CF}_3\text{CFHCFCF}_2\text{CF}_3$

A wet-ice/acetone chilled 150 ml beaker was loaded with 3.17 g of potassium  
30 carbonate (23 mmol) dissolved in 5 ml distilled water, 78 ml of  $\text{CF}_3\text{CFHCFCF}_2\text{CF}_3$ , and 2.35 ml of 30% aqueous hydrogen peroxide (23 mmol). A nominal 100 watt titanium ultrasonic horn was lowered into the reaction mixture now chilled to  $-5^\circ\text{C}$  and then 4.20 g of 4H5Cl (20 mmol) added  
all at once. After an additional 45 seconds of ultrasonication, the reaction mixture  
35 was transferred to a separatory funnel prechilled to  $\sim -15^\circ\text{C}$ . The lower organic phase, milky white in appearance, was separated and its volume measured as

74 ml. Iodometric titration found the concentration of 4H5P 2 to be 0.107 M for a yield of 79% based on starting acid chloride 4H5Cl.

G. Use of Trifluoroacetic Acid to Clear Peroxide Solution

The solution made in part C above was milky in appearance and has to be used immediately if precipitates are to be avoided over the course of long-term, low-temperature storage. Adding trifluoroacetic acid causes most of the haze to clear. A 0.107 M 4H5P solution diluted down with 20% its volume of trifluoroacetic acid stayed clear at -78°C for the 15-30 minutes required to set up for polymerization experiments G and H below.

Adding trifluoroacetic acid appears to speed up the rate of peroxide thermal decomposition. Fifteen milliliters of trifluoroacetic acid were added to 64 ml of the 0.107 M 4H5P solution prepared above in part C causing the milky solution to go largely clear. This mixture was maintained at 0°C in a constant temperature bath while samples were periodically withdrawn for iodometric titration with the results shown below in Table 1.

TABLE 1

Time, second	Molarity, 4H5P <u>2</u>	Nominal Half-Life
0	0.107	
1800	0.085	1.5 hr
3600	0.063	1.3 hr
7200	0.046	1.6 hr
10800	0.040	2.1 hr
18300	0.030	2.7 hr

Treating each peroxide titration as a single point in first-order kinetics, half-life starts off at about 1.5 hours and then drifts to longer times. Polymerization is still initiated after dilution of the peroxide solution with trifluoroacetic acid (see Parts J and K below).

H. Initiation of TFE Polymerization, Carbon Dioxide Reaction Medium

An autoclave prechilled to -37°C was loaded with 5 ml of 0.107 M 4H5P 2 in CF<sub>3</sub>CFHCFHCF<sub>2</sub>CF<sub>3</sub> solvent. The autoclave was evacuated, filled with 50 g of tetrafluoroethylene (TFE) and 150 g of carbon dioxide and allowed to warm towards room temperature. The autoclave was shaken overnight passing through a maximum of 1131 psi at 31°C. Venting gave poly(tetrafluoroethylene) as a white powder that weighed 41.8 g after drying over a weekend in a 150°C vacuum oven.

I. Initiation of TFE/E Polymerization, Carbon Dioxide Reaction Medium

An autoclave prechilled to  $-42^{\circ}\text{C}$  was loaded with 5 ml of 0.107 M 4H5P 2 in  $\text{CF}_3\text{CFHCFHCF}_2\text{CF}_3$  solvent. The autoclave was evacuated, filled with 50 g of tetrafluoroethylene (TFE), 14 g of ethylene, and 150 g of carbon dioxide and  
5 allowed to warm towards room temperature. The autoclave was shaken overnight passing through a maximum of 1010 psi at  $31^{\circ}\text{C}$ . Venting gave white polymer that weighed 39.5 g after drying over a weekend in a  $150^{\circ}\text{C}$  vacuum oven.

J. Initiation of TFE Polymerization, Carbon Dioxide Reaction Medium,  
 $\text{CF}_3\text{COOH}$  added to Initiator Solution

10 An autoclave prechilled to  $-44^{\circ}\text{C}$  was loaded with 5 ml of 0.105 M 4H5P 2 in  $\text{CF}_3\text{CFHCFHCF}_2\text{CF}_3$  solvent to which 1.25 ml of  $\text{CF}_3\text{COOH}$  had been added to eliminate haze and precipitates. The autoclave was evacuated, filled with 50 g of tetrafluoroethylene (TFE) and 150 g of carbon dioxide and allowed to warm  
15 towards room temperature. The autoclave was shaken overnight passing through a maximum of 1084 psi at  $28^{\circ}\text{C}$ . Venting gave poly(tetrafluoroethylene) as a white powder that weighed 38.7 g after drying over a weekend in a  $150^{\circ}\text{C}$  vacuum oven.

K. Initiation of TFE/E Polymerization, Carbon Dioxide Reaction Medium,  
 $\text{CF}_3\text{COOH}$  added to Initiator Solution

20 An autoclave prechilled to  $-56^{\circ}\text{C}$  was loaded with 5 ml of 0.105 M 4H5P 2 in  $\text{CF}_3\text{CFHCFHCF}_2\text{CF}_3$  solvent to which 1.25 ml of  $\text{CF}_3\text{COOH}$  had been added to eliminate haze and precipitates. The autoclave was evacuated, filled with 50 g of tetrafluoroethylene (TFE), 14 g of ethylene, and 150 g of carbon dioxide and  
25 allowed to warm towards room temperature. The autoclave was shaken overnight passing through a maximum of 1095 psi at  $29^{\circ}\text{C}$ . Venting gave white polymer that weighed 15.3 g after drying over a weekend in a  $150^{\circ}\text{C}$  vacuum oven.

EXAMPLE 3

Thermal Decomposition of Initiators at Different Temperature

When n and m are both 1, structure I may be represented by the designation 4H5P (2). When both n and m are 4, structure I may be represented  
30 by the designation 4H8P (3). Both of these peroxides demonstrate very short half-lives compared to the initiators currently used in fluorocarbon polymerization.

Half-lives of initiators are generally determined by placing the peroxide solution in a constant temperature bath and following the peroxide concentration  
35 as a function of time by iodometric titration. The initiator 4H5P has a half-life of 4.4 hr at  $0^{\circ}\text{C}$ , and the initiator 4H8P has a half-life of 7.1 hr at  $0^{\circ}\text{C}$ . These are much shorter than the half-lives of initiators currently used in fluorocarbon polymerization. Examples of the currently-used initiators are heptafluorobutyryl

peroxide (4P), which has a 4.3 hr. half-life at 25°C, and HFPO dimer peroxide (DP, structure 6 in Table 2), which has a 0.98 hr half-life at 30°C. These results are summarized in Table 2 below.

5

TABLE 2

THERMAL DECOMPOSITION OF  $R_f(C=O)OO(C=O)R_f$ 

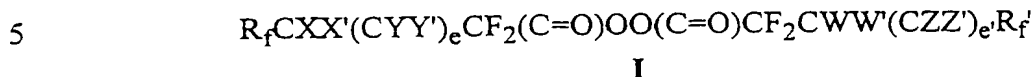
#	$R_f$ GROUP ( $R_f$ and $R_f$ are the same)	NAME	0°C Half-life	10°C Half-life	15°C Half-life	25°C Half-life	30°C Half-life	REF
<u>2</u>	$CF_3CH_2CH_2CF_2-$	4H5P	4.4 hr	1.2 hr				1
<u>3</u>	$C_4F_9CH_2CH_2CF_2-$	4H8P	7.1 hr	1.7 hr				2
<u>4</u>	$HCF_2CF_2-$	1H3P		16 hr		0.85 hr	0.46 hr	3 5
<u>5</u>	$H_2CFCF_2-$	2H3P				0.7 hr		4
<u>6</u>	$CF_3CF_2CF_2OCF(CF_3)-$	DP					0.98 hr	3
<u>7</u>	$CF_3CF_2CF_2-$	4P				4.3 hr	8.8 hr	3

1.  $CF_3CF_2CF_2OCFHCF_3$  solvent was used in this experiment.
2.  $CF_3CF_2CF_2OCFHCF_3$  solvent was used in this experiment.
3. Z. Chengxue, et. al., *J. Org. Chem.*, **47**, 2009 (1982),  $CFCl_2CF_2Cl$  solvent
10. Japanese Patent 61152653 A2, *Chem. Abstracts* **106**:120380
5.  $CF_3CF_2CF_2OCFHCF_3$  solvent was used in this experiment.

CLAIMS

What is claimed is:

1. A diacyl peroxides having the structure I,



wherein e and e' are independently 0 or 1; and

when e = 0, at least one of X, X' is H and any of the other X, X' is H  
10 or F; when e' = 0, at least one of W, W' is H and any of the other W,  
W' is H or F;

when e = 1, at least one of X, X', Y, Y' is H and any of the other X,  
X', Y, Y' is H or F;

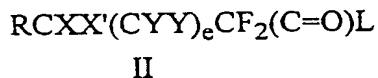
when e' = 1, at least one of W, W', Z, Z' is H and any of the other W,  
15 W', Z, Z' is H or F;

wherein  $R_f = C_n F_{(2n+1)}$ , n = 1 to 4; and

wherein  $R_{f'} = C_m F_{(2m+1)}$ , m = 1 to 4.

2. The diacyl peroxide of claim 1 wherein n and m, independently, are 1  
or 4.

- 20 3. A method for preparing a new class of diacyl peroxides, comprising:  
contacting at least one acid halide of the formula II



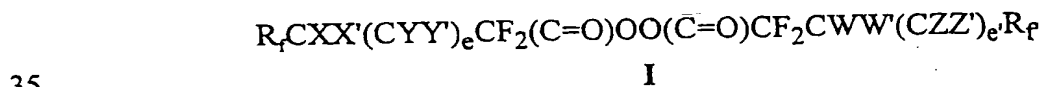
25

wherein e = 0 or 1, and when e = 0, at least one of X, X' is H and any  
of the other X, X' is H or F, and when e = 1, at least one of X, X', Y, Y' is H and  
any of the other X, X', Y, Y' is H or F;

wherein L is Cl or F, and

30 wherein R is  $R_f$  or  $R_{f'}$ ; and wherein  $R_f = C_n F_{(2n+1)}$ , n = 1 to 4 and  $R_{f'} =$   
 $C_m F_{(2m+1)}$ , m = 1 to 4;

with a peroxide, to generate a diacyl peroxide of the structure



wherein e and e' are independently 0 or 1; and

when e = 0, at least one of X, X' is H and any of the other X, X' is H or  
F; when e' = 0, at least one of W, W' is H and any of the other W, W'  
40 is H or F;



when  $e = 1$ , at least one of  $X, X', Y, Y'$  is H and any of the other  $X, X', Y, Y'$  is H or F;

when  $e' = 1$ , at least one of  $W, W', Z, Z'$  is H and any of the other  $W, W', Z, Z'$  is H or F;

5 wherein  $R_f = C_n F_{(2n+1)}$ ,  $n = 1$  to 4; and

wherein  $R_f = C_m F_{(2m+1)}$ ,  $m = 1$  to 4.

4. The method according to Claim 3 wherein the peroxide is selected from the group consisting of  $H_2O_2$  added in the presence of a base,  $Na_2O_2$ , and  $K_2O_2$ .

10 5. The method according to Claim 4 wherein the base is selected from the group consisting of  $NaOH$ ,  $KOH$ ,  $Na_2CO_3$ , and  $K_2CO_3$ .

6. A method for using a diacyl peroxide of the structure I, comprising:



I

15

wherein  $e$  and  $e'$  are independently 0 or 1; and

when  $e = 0$ , at least one of  $X, X'$  is H and any of the other  $X, X'$  is H or F; when  $e' = 0$ , at least one of  $W, W'$  is H and any of the other  $W, W'$  is H or F;

20

when  $e = 1$ , at least one of  $X, X', Y, Y'$  is H and any of the other  $X, X', Y, Y'$  is H or F;

when  $e' = 1$ , at least one of  $W, W', Z, Z'$  is H and any of the other  $W, W', Z, Z'$  is H or F;

25

wherein  $R_f = C_n F_{(2n+1)}$ ,  $n = 1$  to 4; and

wherein  $R_f = C_m F_{(2m+1)}$ ,  $m = 1$  to 4

(i) contacting at least one diacyl peroxide having the structure I with a monomer;

(ii) optionally, in the presence of a reaction medium selected from the group consisting of fluorocarbon, chlorofluorocarbon, and hydrocarbon fluids; fluorocarbon, chlorofluorocarbon and hydrocarbon mixed with water, wherein hybrid polymerization conditions form; and liquid or supercritical carbon dioxide; and

(iii) polymerizing the monomer, under suitable polymerization temperature and pressure whereby fluoroolefin polymerization occurs.

35

7. The method of Claim 6 wherein, independently,  $n = 1$  or 4 and  $m = 1$  or 4;  $e = 1$ ;  $e' = 1$ ; and  $X, X', Y, Y', W, W', Z$  and  $Z'$  are all H.

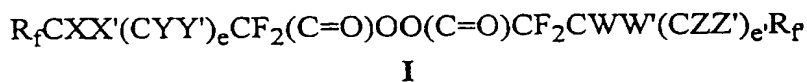
8. The method of Claim 6 wherein the temperature is from about  $-20^{\circ}\text{C}$  to about  $30^{\circ}\text{C}$ .

9. The method of Claim 6 wherein the temperature is from about  $-10^{\circ}\text{C}$  to about  $20^{\circ}\text{C}$ .

5 10. The method of Claim 6 wherein, independently,  $n = 1$  or  $4$  and wherein  $m = 1$  or  $4$ ;  $e = 1$ ;  $e' = 1$ ; and  $X, X', Y, Y', W, W', Z$  and  $Z'$  are all H; and wherein the temperature is from about  $-10^{\circ}\text{C}$  to about  $20^{\circ}\text{C}$ .

11. A process for fluoroolefin polymerization, comprising the steps of:

10 (i) contacting at least one diacyl peroxide having the structure I



wherein  $e$  and  $e'$  are independently  $0$  or  $1$ ; and

15 when  $e = 0$ , at least one of  $X, X'$  is H and any of the other  $X, X'$  is H or F; when  $e' = 0$ , at least one of  $W, W'$  is H and any of the other  $W, W'$  is H or F;

when  $e = 1$ , at least one of  $X, X', Y, Y'$  is H and any of the other  $X, X', Y, Y'$  is H or F;

20 when  $e' = 1$ , at least one of  $W, W', Z, Z'$  is H and any of the other  $W, W', Z, Z'$  is H or F;

wherein  $\text{R}_f = \text{C}_n\text{F}_{(2n+1)}$ ,  $n = 1$  to  $4$ ; and

wherein  $\text{R}_f = \text{C}_m\text{F}_{(2m+1)}$ ,  $m = 1$  to  $4$ ;

with a monomer;

25 (ii) optionally, in the presence of a reaction medium selected from the group consisting of fluorocarbon, chlorofluorocarbon, hydrocarbon fluids; fluorocarbon, chlorofluorocarbon and hydrocarbon mixed with water, wherein hybrid polymerization conditions form; and liquid or supercritical carbon dioxide; and

30 (iii) polymerizing the monomer, under suitable polymerization temperature and pressure whereby fluoroolefin polymerization occurs.

12. A product of the process of Claim 11.

# INTERNATIONAL SEARCH REPORT

In: .tional Application No  
PCT/US 00/23222

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C07C409/34 C08F4/34 C08F114/26 C08F214/26

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C07C C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  
CHEM ABS Data, BEILSTEIN Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 186 215 A (DAIKIN INDUSTRIES LTD) 2 July 1986 (1986-07-02) example 4	12
A	the whole document	1,3,4,6, 8,9,11
X	US 5 182 342 A (A.E. FEIRING ET AL) 26 January 1993 (1993-01-26) examples	12
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

26 October 2000

Date of mailing of the international search report

13/11/2000

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# INTERNATIONAL SEARCH REPORT

In International Application No

PCT/US 00/23222

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>           DATABASE CHEMABS 'Online!            CHEMICAL ABSTRACTS SERVICE, COLUMBUS,            OHIO, US;            STN, CAPLUS accession no. 1987:120380,            XP002150809            cited in the application            abstract            &amp; JP 61 152653 A (DAIKIN INDUSTRIES LTD)            11 July 1986 (1986-07-11)            cited in the application            -----         </p>	<p>           1,3,4,6,            11         </p>

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Information on patent family members

International Application No

PCT/US 00/23222

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